Surface reconstructions on the (100) CoSi$_2$ surface

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Abstract

We have investigated the relative stability of a number of p(1 × 1), c(2 × 2) and p(2 × 2) surface reconstructions on the (100) CoSi$_2$ surface as deposited on Si(100). The relative stability of these reconstructions as a function of whether the growth conditions are either Si rich or Co rich is also investigated. We show that the most stable surface under all growth conditions is a c(2 × 2) reconstructed Si-terminated surface. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

CoSi$_2$ is an attractive self-aligned silicide for the microelectronics industry [1], because of the low lattice mismatch with silicon (~−1.2%) and low electrical resistivity (~14 μΩcm). However, epitaxial CoSi$_2$ films of high structural quality have only been found to grow on the Si(111) surface. Growth on the technologically more important Si(100) surface leads to misorientated grains [2,3]. Recent scanning tunnelling microscopy (STM) experiments of CoSi$_2$ growth on the Si(100) surface [3,4] have revealed a number of different surface reconstructions, as well as the formation of small three-dimensional (3-D) islands. It is essential for the semiconductor industry to be able to grow flat layers for use as metallic contacts, and the 3-D islands are of interest as potential quantum structures. Since surface reconstructions generally play a key role in the growth mechanisms, we have modelled a number of candidate surface reconstructions in order to account for the experimentally observed surfaces of CoSi$_2$(100) on Si(100).

2. Computational details

All the calculations were performed using the CASTEP code [5–7]. The CASTEP code is based on the iterative diagonalization of the Kohn-Sham Hamiltonian [8] in a plane wave basis using the ultrasoft pseudopotentials of Vanderbilt [9]. These have been shown to give good results for CoSi$_2$ while allowing a low energy cut-off to be used [10]. For all the calculations an energy cut-off of 360 eV was used, as this was found to give well-converged energies and forces.
The $k$-points used in the calculations were generated according to the scheme of Monkhorst and Pack [11]. For the bulk calculations an $8 \times 8 \times 8$ $k$-point mesh was used for the 12-atom unit cell. For the surface studies an $8 \times 8 \times 1$ $k$-point mesh was used for the p(1$\times$1) surface unit cell; this was shown to give well-converged results when compared with calculations with a $14 \times 14 \times 1$ $k$-point mesh, with the surface energy changing by less than 6 meV Å$^{-2}$. The calculations were performed in the local density approximation (LDA) [12,13].

The surface calculations were performed at a lattice parameter of $5.32 \text{ Å}$, which represents a 1.2% expansion of the equilibrium theoretical lattice parameter; to simulate the effect of the strain due to the lattice mismatch when deposited on silicon.

In principle, the unreconstructed (100) surface of CoSi$_2$ could be either silicon terminated or cobalt terminated. It has been speculated, with some justification, that the surface termination will always be silicon [14]. We have performed calculations on the unreconstructed surface for both terminations to investigate their relative stabilities. As well as these two surfaces, a number of c(2$\times$2) and p(2$\times$2) surface reconstructions have been investigated; these two reconstructions are the most widely observed reconstructions on the surface.

When constructing a simulation cell to investigate the surface energies for these surface terminations it is not possible to create a stoichiometric cell, the only stoichiometric cell that can be created has one surface cobalt terminated with the other silicon terminated. Therefore, if one wants to calculate the surface energies of these different surfaces, the chemical potential of the atoms must be defined in some way. If we take the silicon, then its chemical potential must lie between that of bulk silicon and the chemical potential of bulk silicon minus the heat of formation of CoSi$_2$ [15].

For the calculations, what we have done is to define the chemical potential of the Si atoms to be that of a bulk Si atom. The idea behind this is that growth is taking place on an Si surface, which is where the Si to make up the CoSi$_2$ comes from, and thus the growth conditions are silicon rich. CoSi$_2$–Si(100) can, however, be grown using either a Co flux alone, or by codeposition of Co and Si.

The growth method used will affect the extent to which the growth occurs under Co- or Si-rich conditions by changing the surface concentrations of species and the source of the species; thus, we have also calculated the range of results that are obtained if we take the growth conditions to be anything from Co rich to Si rich.

3. Results

The calculated lattice parameter $a_0$ and bulk modulus $B_0$ for bulk CoSi$_2$ can be found in Table 1. These are in reasonable agreement with experiment, though the lattice parameter is 2% too small, which is typical of the LDA error. The level of the agreement with the FLAPW calculations of Stalder et al. [10] is very good, indicating that the errors arising from the use of pseudopotentials are small.

The various candidate surface reconstructions are illustrated in Fig. 1. The black circles represent the cobalt atoms, the white circles the silicon atoms; the grey circles represent atoms that can be either silicon or cobalt atoms; the diameter of a circle represents its distance from the surface (the smaller ones are further away). The smaller dashed box represents the p(1$\times$1) unit cell for the case of the silicon-terminated surface. The c(2$\times$2) unit cell is in the centre with the V,2 × 2, R45° cell used in the simulations shown by the dashed box. The p(2$\times$2) unit cell is to the right and is composed of the four squares with silicon atoms at the corners.

<table>
<thead>
<tr>
<th></th>
<th>$a_0$ (Å)</th>
<th>$B_0$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CASTEP</td>
<td>5.26</td>
<td>197</td>
</tr>
<tr>
<td>FLAPW [10]</td>
<td>5.292</td>
<td>201.8</td>
</tr>
<tr>
<td>VAMP [10]</td>
<td>5.283</td>
<td>200.2</td>
</tr>
<tr>
<td>Experiment [16]</td>
<td>5.365</td>
<td>171.5 ± 3.4</td>
</tr>
</tbody>
</table>

Table 1

Bulk properties of CoSi$_2$ as calculated in the present work and in the work of Stalder et al. [10] compared with experiment [16]. $a_0$ is the lattice parameter in Ångströms, $B_0$ is the bulk modulus at the equilibrium lattice constant. The full-potential linear augmented plane wave (FLAPW) calculations and the plane wave pseudopotential calculations using the Vienna ab initio molecular-dynamics program (VAMP) are from the work of Stalder et al. [10].
For all the relaxations the forces were relaxed until they were less than 0.01 eV Å⁻¹, this gives bond lengths that are correct to less than 0.01 Å. There is a systematic error due to the tendency of the LDA to overbind, which means that the Co–Si bond distance is some 0.04 Å too short and the Si–Si bond distance is some 0.02 Å too short, as is evidenced by the theoretical CoSi₂ lattice parameter being too small. However, in the discussions of the results below it is the trends in the results that are more important than the absolute lengths.

The simulation cell for the p(1×1) silicon-terminated case contained six layers of silicon and five of cobalt; for the cobalt-terminated case the cell contained five layers of silicon and six of cobalt; in both these cases the silicon layers contain two atoms, and the cobalt one. The surfaces were separated by a 13 Å vacuum layer.

The surface energy of the silicon-terminated unreconstructed surface is 114 meV Å⁻², with the surface silicon atoms relaxing only 0.04 Å downwards from their bulk positions. For the case of the cobalt-terminated surface the surface energy is 222 meV Å⁻², with the surface cobalt atoms relaxing 0.13 Å downwards. It can be seen from these results that the calculated surface energies strongly support the conjecture that the surface is silicon terminated in a silicon-rich environment; in fact, as we will see later, this also holds true under cobalt-rich conditions.

There is a further candidate p(1×1) surface structure that is of interest, particularly in comparison with the c(2×2) and p(2×2) reconstructions that we discuss below. This is formed by taking the cobalt-terminated surface and replacing the cobalt atoms with silicon atoms. The details for the simulation of this surface are the same as the previous two p(1×1) surface reconstructions. This surface has a surface energy of 84.9 meV Å⁻², with the surface silicon atoms relaxing 0.30 Å upwards in comparison with the bulk positions of the cobalt atoms.

The surface reconstruction most commonly observed experimentally on the CoSi₂(100) surface is the c(2×2) reconstruction [3,4,14]. A possible surface reconstruction to account for this proposed by Stalder et al. [14] involved the silicon atoms moving together to form a delocalized bond (see fig. 7 of Ref. [14]). This surface reconstruction has subsequently been shown by the same authors, by the use of ab initio calculations, not to be stable [17]. We also find this to be the case; the energy gained by the saturation of the dangling bonds due to the delocalized bond is far outweighed by the cost of reducing the Si–Co–Si bond angle.

All other proposed surface reconstructions involve the addition of an extra half or a quarter layer of atoms onto the silicon-terminated surface. These forms the c(2×2) and p(2×2) reconstructions, which are illustrated in Fig. 1. It has been proposed that these additional atoms would be silicon atoms and there have been two sets of calculations that have investigated these reconstructions [17,18]. Stalder et al. [17] calculated...
simulated STM images of the unrelaxed silicon-terminated c(2×2) surface would look like. Voigtla¨nder et al. [18] investigated a surface that was composed of cobalt and silicon in a mixed-terminated p(2×2) cell. This work argued that if the cobalt and silicon were randomly distributed in these sites then surface diffraction techniques would see the surface reconstruction as a c(2×2) reconstruction. They then utilized voltage-dependent STM to differentiate between surface cobalt and silicon atoms, tying this in with some calculations performed on the mixed-terminated cell. Neither of these studies included the relaxation of the surface atoms in the modelling.

Our calculated surface energies for the c(2×2) and p(2×2) surface reconstructions can be found in Tables 2 and 3, with the grey circles in Fig. 1 being silicon or cobalt.

For the c(2×2) surfaces the simulation cell used was a $\sqrt{2} \times \sqrt{2} \times 45^\circ$ cell that contained six layers of silicon and five layers of cobalt with an additional layer occupying half the sites that the next cobalt layer would have occupied on both surfaces in the cell. A 6×6×1 Monkhorst-Pack mesh was used for the k-point sampling. For this case the cell with an extra half layer of silicon is found to be, by far, the most stable structure in the silicon-rich environment. The unusual environment of the surface silicon atom leads to an upward relaxation of the silicon atom by 0.18 Å; the cobalt, when placed in this environment, relaxes downwards by 0.17 Å (both these distances refer to the relaxation relative to what the bulk cobalt position would have been).

For the p(2×2) cell we have considered three different cases consisting of a surface where an additional quarter layer of atoms in the next cobalt sites are either (i) silicon or (ii) cobalt and (iii) the case where we have an additional quarter layer of silicon and cobalt (this is identical to the system studied in Ref. [18]). For all these cases, a system containing four layers of silicon and three layers of cobalt was used with the cell dimension in the z-direction being 25 Å. A 6×6×1 Monkhorst–Pack mesh was used for the k-point sampling. The results are presented in Table 3, where case (i) with an additional quarter layer of silicon indeed proved to be the most stable of these surfaces. The energy of the mixed-terminated surface is close to that of the purely silicon-terminated case, thus indicating that the mixed-terminated surface may well play a role in the growth of the surface.

Although the bonding environment of the additional atoms on the surface is a natural one for cobalt, it is not for silicon. The bonding gives the surface atom a fourfold coordination, but the bond angles are those of an atom in an eightfold-coordinated position. In the relaxation of the mixed-terminated surface the cobalt atoms sit 0.33 Å lower than the silicon atoms. This is important for the simulation of the STM images, though it is not the atom geometry alone that an STM tip ‘sees’, but the surface electronic structure.

There is a general trend in the layer separation between the final layer and the layer below for all the different surface terminations. In the case of the Si p(1×1) surface the silicon atoms relax a very small amount downwards in comparison with the bulk layer separation; these silicon atoms are bonded to two cobalt atoms in the layer below. The cobalt atoms in the p(1×1), c(2×2), p(2×2) and mixed p(2×2) cases relax ~0.14 Å further from the surface than the bulk layer separation would give; in all these cases the silicon atoms are bonding to underlying silicon atoms.

These silicon atoms have a longer Si−Si bond
length than in diamond silicon, in which the silicon atoms are similarly fourfold coordinated; the bond lengths here are 2.42 Å in comparison with 2.33 Å in diamond silicon. For the case of the p(1 × 1) surface, with silicon substituted for cobalt, the silicon atoms are further away again at some 0.30 Å from the bulk cobalt positions; this also makes the Si–Si bond lengths longer at 2.48 Å. The bonding configuration of the silicon atoms can be seen in Fig. 2.

The work of Voigtländer et al. [18] used a combined ab initio experiment approach in order to identify surface atoms chemically. The one failing of the work was not to allow for the effect of the relaxation of the surface atoms in the modelling work. Given that we have shown that the cobalt atoms sit some 0.33 Å lower than the silicon atoms on the mixed-terminated surface, it is important to assess the impact of this on the simulated STM images, and thus the match with what is seen by experiment. The simulated STM images can be seen in Fig. 3. It is clear from this picture that the conclusions of the work by Voigtländer et al. [18] are unchanged by the surface relaxations. The simulated STM images have been generated using the method of Tersoff and Hamann [19] at 0.5 and 1.0 V positive bias (i.e. tunnelling into the surface).

If we investigate the effect of changing the chemical potential of the silicon by assigning the effect of the relaxation of the surface atoms in the heat of formation energy to the chemical potential of the silicon atoms then we can investigate different growth conditions. The results can be seen in the graph in Fig. 4, where the experimental heat of formation of 1.02 eV CoSi$_2$ has been used. Increasing the chemical potential of the silicon changes the stable surface to the c(2 × 2) silicon-terminated reconstruction. At the cobalt-rich end of the graph there are a number of surfaces that are close in energy.

4. Summary

Under silicon-rich growth conditions cobalt-terminated surfaces are energetically highly unfavourable. This supports the models that have been proposed for the CoSi$_2$ (100) surface. In the limit of silicon-rich conditions the favoured surface reconstruction should be the p(1 × 1) surface with the cobalt atoms replaced by silicon atoms. However, the surface with a half layer of silicon that forms the c(2 × 2) reconstruction is energetically indistinguishable from this within the errors of the calculation; the energy difference in the calculations is 0.02 eV per surface in the c(2 × 2) cell. Also, if we start to assign any of the heat of formation energy to the silicon atoms then the c(2 × 2) reconstruction immediately becomes the more stable surface. In the limit of the cobalt-rich case the Si c(2 × 2) reconstruction is still some 0.45 eV per c(2 × 2) cell lower in energy than the most favourable cobalt-terminated case. Therefore, it is likely that surfaces that are seen as c(2 × 2) reconstructed in the experiments are half silicon-terminated surfaces.

The mixed-terminated p(2 × 2) surface, which was proposed as being important in the growth
Fig. 3. Simulated STM images of the mixed-terminated \( p(2 \times 2) \) surface reconstruction at (a) 0.5 and (b) 1.0 V. Both the silicon (lighter atom) and cobalt (darker atom) show on the image at 0.5 V, whereas cobalt (darker atom) alone is visible at the higher imaging voltage.
of CoSi$_2$ on Si (100) by Voigtlaender et al. [18], is not much higher in energy, particularly in the cobalt-rich regime. As neither the growth nor the final surface structures observed in such experiments are necessarily in equilibrium, the mixed-terminated p(2 × 2) surface may well be present. The evidence from the STM image simulations (see Fig. 3) indicates that the conclusions of Voigtlaender et al. [18] hold even with the cobalt atoms some 0.33 Å lower than the surrounding silicon atoms.

The silicon bonding in these systems is of great interest owing to the very unusual bonding configuration taken by the silicon atoms in these structures. This has consequences for the energetics of the surfaces. From a simple bonding argument you could argue that the p(1 × 1) surface where the cobalt atoms have been substituted by silicon atoms would be much lower in energy than the silicon c(2 × 2) surface, because in the p(1 × 1) case all the dangling bonds would be saturated whereas for the c(2 × 2) case only half are. This behaviour is certainly seen in the energy difference between the silicon c(2 × 2) and p(2 × 2) cases, which saturate a half and a quarter of the dangling bonds respectively. However, the calculations show these surfaces to be very close in energy. The reason can be seen by looking at the relaxations of atoms in the surface layer and the layer below. For the c(2 × 2) case the silicon atoms in the next-to-top layer that are bonded to have some freedom to relax, and they do so by moving so as to increase the Si–Si(top)–Si bond angle; this allows a shorter, and hence stronger, bond to be formed than in the case of the p(1 × 1) structure (where this relaxation is not possible by symmetry). So the saturation of more dangling bonds is energetically offset by the stronger bonds that are formed.

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